ELASTIC AND THERMAL ANALYSIS OF CLAY/POLYMER NANOCOMPOSITE MATERIAL

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Elastic and thermal analysis of clay/polymer nanocomposite material

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This is to certify that the work presented in the dissertation entitled "**Elastic and thermal analysis of clay/polymer nanocomposite material"** submitted by ***Arvind Kumar Thakur,*** Roll Number 214ME1305, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Technology* in *Mechanical Engineering*. Neither this dissertation nor any part of has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

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Prof. J. Srinivas

Associate Professor

DECLARATION OF ORIGINALITY

I, Arvind Kumar Thakur, roll no. 214ME1305 hereby declare that this dissertation entitled **"Elastic and thermal analysis of clay/polymer nanocomposite material"** represents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section "References". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

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ABSTRACT

Composites are the new type of emerging material that promise the improved properties. The mechanical properties of nanocomposites are achieved by the reinforcement of fiber into the matrix. In the present days every industry need to develop a new class of material with improved mechanical properties, low weight, high wear resistance etc. The basic objective of the nanocomposite to optimize its design to develop new cost efficient material. This work gives a methodology of finding effective elastic properties of nano-clay-reinforced polymer composites with aligned and randomly oriented clay platelets. When interphase regions exist between nanoclay platelets and polymer, numerical homogenization is initially required to identify the properties of effective particle consisting of both clay and interface regions. Once the elastic properties of equivalent particle are obtained, empirical methods like Mori-Tanka and Halpin-Tsai approach are employed to identify all the effective properties of resultant composite. The methodology is implemented with a modular based computer program developed in MATLAB and the variation of longitudinal modulus as a function of weight fraction of nanoclay, aspect ratio of fibers, number of stacks, nanoclay volume fraction etc is reported. In this work, mechanical reinforcement of MMT clay platelets in widely used nylon-6 and MXD6 polymer matrices is employed. As second computational approach, the effective elastic properties of clay/polymer nanocomposite for uniform and randomly oriented clay particles are determined by using 3D cylindrical and 2D square representative volume element (RVE) method respectively. The effect of the volume fraction of nano-clay platelets on the mechanical behavior of RVEs was studied. Large surface area of nano-clay platelets contributes the stiffening effect of nanocomposite. As next study,CNT polymer composite reinforced with nanoclay platelets is considered and the analysis of this hybrid composite is attempted again in two ways (micromechanical modeling and by finite element method). The micromechanical results are validated with the finite element result and with published data. An experimental study is conducted on thin samples of polymer and polymer nanoclay composites to test the tensile and flexural modulus.

Keywords: Nanoclay, CNT, Halpin-Tsai&Mori-Tanka model, RVE, Nylon, Epoxy.

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Nomenclature

1	V_s	Volume fraction of nanoclay in composite
2	V_m	Volume fraction of matrix
3	v_S	Volume of nanoclay
4	v_C	Volume of nanocompoaite
5	α	Volume fraction of nanoclay in effective particle
6	E_S	Elastic modulus of nanoclay
7	E_I	Elastic modulus of interphase
8	E_P	Elastic modulus of effective particle
9	υ	Poisson's ratio
10	G	Shere modulus
11	N	Number of stacks
12	d_s	Nanoclay thickness
13	d_p	Effective particle thickness
14	E	Elastic modulus of nanocomposite
15	K	Thermal conductivity of nanocomposite
16	V_p	Volume fraction of effective particle
17	ε	Strain
18	ϕ	Volume fraction of CNT in effective CNT particle
19	p	Elastic modulus of hybrid composite
20	σ	Stress
21	C	Transfer matrix coefficient
22	γ	Shere strain
23	u	Displacement
24	$\varepsilon_1, \varepsilon_2$	Empirical constant in Halpin-Tsai model depends on fiber shape

Chapter 1

INTRODUCTION

1.1 Overview

The fiber reinforced polymer nanocomposite materials made up of three basic phase matrix, fiber and the fine interphase region. The fibers are reinforcing in the matrix material improve its properties like mechanical, thermal and electrical. The reinforcing materials are in discontinuous phase and the matrix materials are in continuous phase. The third phase in the nanocomposite is interphase which has properties between fiber and matrix materials. Fibers have more strength than the matrix material in nanocomposite. In the nanocomposite material one of the dimension of fibers or reinforcing materials are in nanoscale within the range 1nm to 100 nm. In this work we have used the polyamide (NYLON 6) as matrix material and clay (Montmorillonite) as a reinforcing material. The fibers are providing the stiffness and strength in the nanocomposite whereas the matrix material related to the thermal properties. The polymer matrix materials are basically of two types thermosetting and thermoplastic. The reinforcing materials are made up of particles, sheets and fibers. The surface area to volume ratio of fiber also called aspect ratio is very high, reinforcing in the matrix gives the improved properties than the individual phase of nanocomposite material. Polymeric materials are used in several applications due to their low cost and ease of fabrication. In order to improve their mechanical properties and high-temperature resistivity, polymers are reinforced with particles or fibers. Nanofibers when inserted at low volumes would drastically improve the performance of the polymers. In order to predict effective properties, multiscale approaches can be used appropriately. Any matrix inclusion based micromechanical model can predict the elastic properties. Recently, nanoclay reinforced polymers are one of the most widely used nanocomposites. They have high aspect ratio and higher contact area. When there are low weight percentages of nano-clay, then Halpin-Tsai analytical model can be used effectively. On other hand finite element models give the result close to the experiments even at higher volume fractions. When volume fraction increases, elastic modulus rises up to a threshold value. After this point the elastic modulus will decrease.

However the analytical methods indicate an increasing trend always with volume fraction. Due to the interface between the nano-clay and matrix (imperfect bonding), stress concentration-effects may reduce the elastic modulus after the threshold level so the interfacial de-bonding between the nano-particles and matrix has to be considered during modeling. The efficiency of properties improvements depends strongly on the properties (mechanical) of the filler, the adhesion between matrix and filler and especially on the aspect ratio of the filler. The aspect ratio of the filler is very important and crucial for many properties in composite such as electrical. In this context, it is appropriate to predict the elastic and thermal properties of nanoclay reinforced polymer composite materials using computational techniques such as empirical models and finite element analysis.

1.2 Matrix materials

Matrix materials are the continuous material in which the reinforcements are embedded. There are many types of matrix material like metal, polymer, ceramics, alloy, cements etc. These all types of matrix material play an important role in the nanocomposite field and enhance the performance of composite. The properties of nanocomposite also depend upon the reinforcing materials and on its shape. Thermoplastic and thermosetting resins, there are two types of polymer matrix material. Thermoplastic resins are solid at ambient temperature and it melt above a specific temperature and then it's converted into a solid after cooling. Thermosetting resins are heated once and it can not be shaped again and again. The thermoplastic resins are polyamide, polypropylene, polythene, polyethylene terephthalate, polystyrene where as thermosetting resins are epoxy, polyester, Melamine formaldehyde can provide the better strength to nanocomposite. The nylon and epoxy polymer matrix material enhance the mechanical, thermal and electrical properties because these materials have better characteristics and it more used in the nanocomposite field industries. The low properties of polymer matrix material can be improved by reinforcing the fiber into it.

1.3 Reinforcements

The purpose of the reinforcing material into the polymer matrix resins is to improve the mechanical and thermal characteristics of neat polymer material. The reinforcements are in the form of fiber, particles and whiskers. The fibers are of different type and having different properties, reinforcing into the polymer matrix to form nanocomposite of different characteristics. The different types of continuous material such as clay, glass fiber, carbon fiber etc. are used as reinforcements. The properties of nanocomposite depend upon fiber properties, orientation of fibers, interaction and amount of reinforcement with polymer matrix as weight or volume fraction.

1.4 Clay

In present world, the clay plays important role as reinforcing material and it is used by many manufacturing industries. Clay is a fine-grained soil material and it consists of one or more clay minerals with traces of oxides of metal and organic material which has high strength and stiffness. The clays are plastic in nature with water molecules and it get hardened after heating. Clays have small size than other natural soil. Some examples of nanoclay platelets are cloisite20A, montmorillonite (MMT) clay which is the member of smectite group etc. The montmorillonite clay is formed by two tetrahedron sheets of silica and one octahedron sheet of alumina. It has good mechanical and thermal characteristics.

1.5 Polymer matrix nanocomposite (PMNC)

Polymer matrix nanocomposites are the most common nanocomposites now days applications. The thermosetting and thermoplastic materials used as matrix material as polyamides, epoxies etc and reinforcing materials are, CNT,grapheen ,clay ,glass and carbon fibers. The polymer matrix nanocomposite material properties depend upon the size of the fiber, orientation and amount of fiber. It also depends upon the aspect ratio of the reinforcing material. This nanocomposite is very popular in now a day due to their low cost and simple fabrication technique. Polymer matrix possesses the specific properties like low coefficient of thermal expansion, elasticity and it should also have flow properties that it penetrates into the fiber easily. The most important moulding process for polymer matrix nanocomposites is hand layup, Spray up moulding, injection moulding and press moulding. This is used in various applications like construction, aerospace components, and chemical plants and in mechanical engineering components.

1.6 Types of polymer matrix nanocomposite

Different classes of nanocomposites come into existence.These are briefly explained.

1.6.1 On the basis of nature of fiber reinforcement

Fig.1.1 shows that the types of nanocomposite on the basis of fiber reinforcement nature in which the fiber embedded into the matrix as particle, short fiber and as continuous fiber or long fiber.

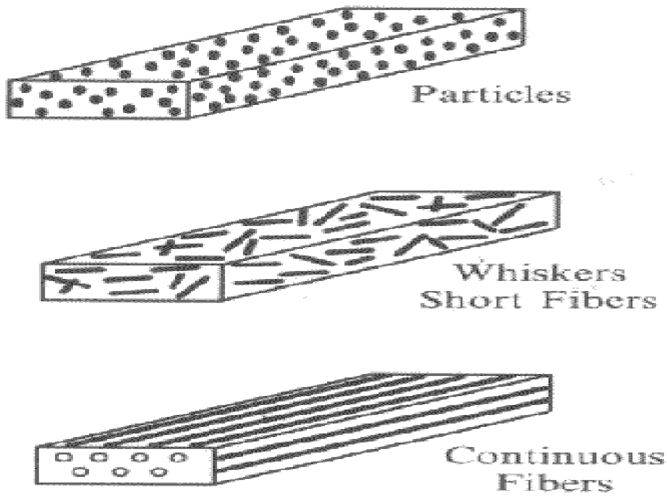

Fig.1.1 Types of polymer nanocomposite on the basis of fiber reinforcement nature.

In the particle reinforced nanocomposite, the orientation of fibers are not controlled and it's like a dimensionless, at microscale it can be seen. But in continuous and short reinforcing the fiber has dimension.

1.6.2 On the basis of insertion of fiber

(a) Phase separated morphology (micro composite)
(b) Intercalated morphology (nanocomposite)
(c) Exfoliated morphology (nanocomposite)

Fig.1.2 shows that the various structures of nanocomposite with respect to the insertion of the nanoclay fiber into the polymer matrix. If the polymer chain can't penetrate into the fiber arrangement and the fiber will not disturb then it is called phase separated morphology.It behaves like micro-composite, where as when the polymer chain penetrates into the layers of clay platelets such that inter layer spacing between clay particle is expanded but layers have well defined arrangement called intercalated morphology. In exfoliated morphology the individual clay layers are randomly distributed into the polymer chain and the arrangement of the clay particle is disturbed.

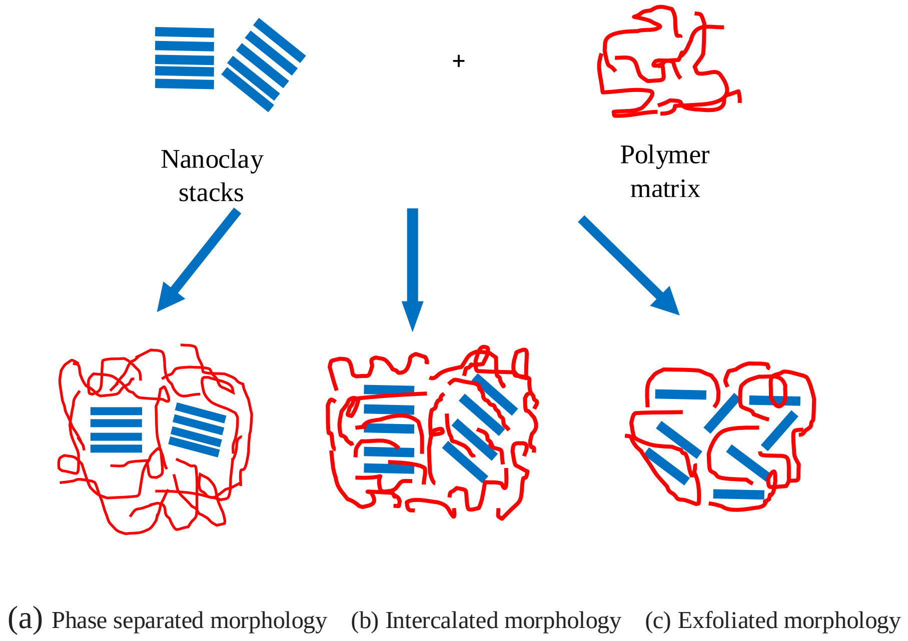

Fig.1.2 Nanoclay reinforced polymer composite structure

In the exfoliated morphology, interphase is created around the nanoclay platelets where as in the intercalated morphology the interphase thickness is assumed to be negligible as compared to the stack thickness, due to the penetration of polymer chain into the nanoclay layers, a interlayer spacing is created which is called gallery.

1.7 Hybrid composite

Hybrid composite materials have the two constituents at the molecular or nanometer level with quite different properties. The different materials cannot dissolve easily into each other. Commonly one of these fibers is inorganic in nature and the other one organic in nature. In the hybrid composite, one fiber overcomes the limitations of other. The organic fiber shows bonding between the polymer matrix and fibers where as inorganic fiber gives the mechanical strength to the composite. The hybrid composites are the new class of material which are used in the several applications like aerospace, automobile, structural engineering and many more. The hybrid composites are the more efficient than the nanocomposites and conventional composites in respect of its properties like mechanical, thermal and electrical. The fiber inserted into the polymer matrix is continuous, discontinuous or short fiber and in the particle form.

1.8 Objectives of present study

Following are the objectives of present work

- Evaluation of the effective elastic modulus of clay fiber reinforced polymer nanocomposite by using micromechanical modeling (Mori-Tanka model and Halpin-Tsai model) and finite element modeling of alligned and randomly distributed fibers.
- Prediction of effective properties of intercalated morphology by mathematical modeling and by using finite element (2D and 3D RVE) analysis.
- Prediction of effective properties of exfoliated morphology by mathematical modeling and by using finite element (2D and 3D RVE) analysis.
- Analysis of thermal properties by using Halpin-Tsai model.
- Prediction of effective properties of clay/CNT polymer hybrid composite.
- Validation of results from FEM and micromechanical model.
- Carry out an experimental work to obtain elastic properties of clay polymer nanocomposite.

1.9 Thesis outline

The remaining part of the thesis is arranged according to the following headlines.

Chapter 2 describes literature review to give the idea about the research work. It presents the work of previous investigators of clay reinforced polymer composite and hybrid composite about the elastic modulus and thermal conductivity.

Chapter 3 includes the details of mathematical modeling and numerical modeling of clay reinforced polymer nanocomposite and hybrid composite.

Chapter 4 presents the result of micromechanical modeling, numerical modeling on the elastic modulus and thermal conductivity of nanoclay reinforced and hybrid composite.

Chapter 5 gives the conclusions of the thesis and direction for future work.

Chapter 2

Literature Review

Several relevant works on prediction of effective characteristics of nanoclay composites are presented in this chapter.

2.1 Mechanical properties of nanocomposite

The following works describe the nanoclay/polymer composite mechanical properties prediction procedure in a chronological sequence.

Fornes and Paul [1] described about the reinforcement of fiber into the nylon 6 polymer and the properties examined by using composite theories of Mori-Tanka and Halpin-Tsai. Reinforcement shows high modulus of elasticity in respect of aspect ratio, orientation of fiber and its quantity to be reinforced.

Luo and Daniel [2] have shown the characteristics and modeling of mechanical behavior of clay/polymer nanocomposites. The ongoing research shows that the dramatic change in stiffness and thermal properties in these nanocomposites with small amount of fiber concentration. The property of nanocomposite is obtained by taking random and aligned orientation of particles.

Sheng et al. [3] stated that the mechanical properties of reinforced clay/polymer nanocomposites enhanced by reinforcing of very low weight fraction of clay. Its properties mainly depend upon the second stage property of effective particle. Multiscale modeling is done for the analysis of morphology of nanocomposite. The experiment done to evaluate the structural parameter like no. of stacks and inter spacing distance in the particle.

Odegard et al. [4] proposed that the stiffness of nanocomposite is depends upon the radii of the fiber reinforcement and it analysis by micromechanical model. A radius of nanoparticle varies from 1nm to 100 nm and the interface condition has significant effect on the mechanical properties for nanoparticles radii below 100 nm.

Hbaieb et al. [5] studied that the stiffness of nanoclay polymer composite affected by distribution of fiber in the polymer matrix. The aligned particle can be distributed randomly even at higher volume fraction but randomly oriented particle cannot be distributed randomly at higher volume fraction. For randomly oriented particle the Mori-Tanka approach overestimates the effective modulus so we use the Halpin-Tsai model.

Dong and Bhattacharyya [6] analysed the 2D representative volume element (RVE) models, using finite element analysis to obtain the effective elastic properties of nanocomposite material. In this paper a three phase RVE is considered that is an interphase between the fiber and polymer matrix, the properties obtained in respect of clay content, aspect ratio and volume fraction. In this analysis the exfoliated morphology shows more elastic properties than intercalated morphology.

Chan et al. [7] studied the reinforcing mechanism of clay polymer nanocomposite, the effective elastic properties of nanocomposite depends upon the reinforcement of fiber and its orientation in the polymer matrix.

Wang et al. [8] expressed the computational analysis of composite structure on the effective properties. A coding is done to generate the 3D RVE of clay polymer nanocomposite to analysis the elastic properties numerically with three phase structure of different properties. The effects of interface properties, fiber size, fiber shape and volume fraction of nanoreinforcement on the modulus of nanocomposites are studied in numerical experiment.

Baniassadi et al. [9] considered the effect of nanoclay additives on the effective properties such that mechanical and thermal of nanoclay polymer composite. In this we use the statistical continuum theory to obtain the elastic and thermal properties, the results are taken with 1%, 3% and 5% by weight of nanoclay in the composite and it is validated with the experimental result. The analysis has shown the effective elastic modulus increases with small amount of addition of nanoclay in exfoliated morphology.

Zairi et al. [10] studied the effects of size and structural parameters of nanoclay on the yield response of polymer clay nanocomposites using multiscale modeling approach.

Tehrani and Abu Al-Rub [11] employed meso-mechanical modeling of polymer clay nanocomposites using visco-elastic, plastic constitutive model.

Bedoui and Cauvin [12] predicted elastic properties of nanoclay reinforced polymers using hybrid micro-mechanical models.

Pahlavanpour et al. [13] stated the prediction of effective elastic properties using micromechanical model and by using 3D finite element analysis. The predicted elastic characteristics of polymer clay nanocomposite were studied in the function of the thickness and elastic properties of interphase formed around the nanoclay platelets. The effect of interphase was considered in a two-step homogenization procedure that exploits the effective particle concept.

Pahlavanpour et al. [14] predicted the stiffness of clay/polymer nanocomposite with aligned particle by studies the one-step and two-step homogenization model. This study covers the both intercalated and exfoliated morphologies for analysis and results came are compared by RVE analysis on Ansys.

Liu and Huang [15] stated the Mori-Tanka method to analysis the effective longitudinal and transverse elastic properties of nanocomposite material.Mori tanka method overestimate the result obtaining from it for random oriented particle.

Figiel [16] analysed with continuum model to predict the effect of interphase on the behaviour of deformation of clay/polymer nanocomposites during semi-solid state. The interphase exists and has a finite thickness and bonded with each clay platelets on both side.

Gelineau et al. [17] aimed to obtaining the elastic properties of nano-clay reinforced polymer composite by using multi-scale modeling. Platelets thickness and the interspacing distance between the clay platelets in the stacks are considered in the micromechanical modeling.

Zare [18] considered an approach for the obtaining the interfacial properties of nano-clay reinforced polymer composite by the experimental results of yield strength. The effective properties of nanocomposite relates with the various input characteristics such that strength and thickness of interphase, strength of nanoclay, aspect ratio and polymer strength.

Meybodi et al. [19] stated that elastic modulus of nanocomposites are presented, the analysis done with numerical and experimental method. Finite element modeling of effective elastic modulus is employed with or without considering the interfacial debonding between the clay platelets and polymer matrix. In this study assumption of perfect bonding is incomplete.

Razavi et al. [20] predicted thermal mechanical and corrosion resistance properties of vinyl-ester/clay nanocomposite subjected to electron beam.

Thakur and Srinivas [21] analysed the effective elastic properties of aligned clay fiber reinforced polymer nanocomposite using finite element method and by using Mori-Tanka or Halpin-Tsai model.

Nuhiji et al. [22] studied the influence of processing techniques on the matrix distribution and clay filtration in a fiber reinforced nanoclay composite.

2.2 Thermal properties of nanoclay composite

Polymer clay nanocomposites are known for high thermal stability. The improved thermal stability is due to action of clay as insulator. The following some of the related references.

Fukushima et al. [23] analysed the thermal and thermo-mechanical properties taking the effect of nature and content of clay in the polymer matrix. The thermal behaviour of clay polymer nanocomposite is mainly depends upon the aspect ratio and dispersion of clay in the nanocomposite.

Mortazavi et al. [24] developed the theoretical as well as experimental based multiscale modeling for the prediction of effective elastic modulus and thermal conductivity of nanocomposite.

Azeez et al. [25] given a review of background research carried out on epoxy clay nanocomposites. Here both mechanical and thermal property prediction techniques of nanoclay/polymer composites were summarized.

Fitaroni et al. [26] analysed the thermal behaviour of nanocomposite as compared to the polymer matrix. The montmorillonite clay reinforced into the polymer matrix, and its enhanced the thermal stability of nanocomposite. The aim of this work to evaluate the effect of MMT clay in the degradation of composites by using thermo- gravimetric analysis.

2.3 Hybrid composite analysis

Hybrid composites are made by combining two or more different types of fillers in a common matrix.The following are some of the references related to hybrid composites.

Kretsis [27] analysed the mechanical properties like tensile strength, shear strength and flexure properties of hybrid fiber reinforced polymer composite. The results are obtain by experimentally and analysis on numerical software and it validated with each other.

Jia eta al. [28] prepared a novel nanostructure hybrid (SiO2-MWCNTs) polymer composite, in which nano silica particle are grown over CNTs.

Rahmanian et al. [29] demonstrate the FE modeling of carbon nanotube silica reinforced epoxy composite considering that CNTs are grown over micro silica particle.

Gabr et al. [30] predicted mechanical and thermal properties of carbon fiber polypropylene composite filled with nanoclay.

Withers et al. [31] studied the improved mechanical properties of an epoxy glass fiber composite reinforced with surface nanoclays.

Thakur et al. [32] Studied the effective elastic properties of CNT/Nano-clay reinforced polymer hybrid composite by numerical method and micromechanical method using Halpin-Tsai model.

Chapter 3

Modeling

This chapter explains semi-empirical relations and finite element modeling of nanoclay polymer composites.

3.1 Micromechanical Modeling of Clay/Polymer Nanocomposite

3.1.1 Mechanical properties

To predict the effective mechanical properties of nano-clay reinforced polymer composite there are two steps, first step is to obtain the effective properties of nanoclay particle and in the second step effective particle is homogenized with polymer matrix from which we obtain the overall effective properties of nanocomposite. The effective particle is the combination of nano-clay platelets and interphase. For analysis there are several models but we implemented the Mori-Tanka model and Halpin-Tsai model.

Volume fraction of nano-clay in composite is given by

$$V_s = \frac{v_S}{v_C} \quad (1)$$

$$V_m = 1 - V_S \quad (2)$$

Where,

V_s and V_m are the volume fractions of nanoclay fiber and polymer matrix whereas v_S and v_C are the volume of nano-clay platelet and nanocomposite.

Rule of mixture used to obtain the properties of effective particle and then the properties of nanocomposite is obtained by using Mori-Tanka model and Halpin-Tsai model.

$$E_{11} = E_{33} = \alpha E_s + (1-\alpha)E_I = E_P \tag{3}$$

$$E_{22} = \frac{E_S E_I}{\alpha E_I + (1-\alpha)E_S - \alpha(1-\alpha)E_S \beta E_I} \tag{4}$$

$$\upsilon_{12} = \upsilon_{32} = \alpha \upsilon_I + (1-\alpha)\upsilon_S \tag{5}$$

$$\upsilon_{13} = \frac{\alpha \upsilon_S E_S (1-\upsilon_I{}^2) + (1-\alpha)\upsilon_I E_I (1-\upsilon_S{}^2)}{\alpha E_S (1-\upsilon_I{}^2) + (1-\alpha)\upsilon_I E_I (1-\upsilon_S{}^2)} \tag{6}$$

$$G_{12} = G_{32} = \frac{G_S G_I}{\alpha G_I + (1-\alpha)G_S - \alpha(1-\alpha)\eta G_I G_S} \tag{7}$$

$$G_{13} = \frac{E_{11}}{2(1+\upsilon_{13})} \tag{8}$$

Where,

$$\beta = \frac{\upsilon_S{}^2 (E_I / E_S) + \upsilon_I{}^2 (E_S / E_I - 2\upsilon_S \upsilon_I)}{\alpha E_S + (1-\alpha)E_I} \tag{9}$$

$$\eta = \frac{\upsilon_S{}^2 (G_I / G_S) + \upsilon_I{}^2 (G_S / G_I - 2\upsilon_S \upsilon_I)}{\alpha G_S + (1-\alpha)G_I} \tag{10}$$

Volume fraction of nano-clay in the effective particle in terms of no. of stacks in the effective particle.

$$\alpha = \frac{N d_S}{d_P} \tag{11}$$

Here, E, G and ν are elastic modulus, shear modulus and Poisson ratio respectively. The subscripts 1, 2, 3 are Cartesian co-ordinate axes (the platelet thickness is along 2). The subscripts S and I represent nanoclay and interphase respectively. Also, N=number of nano-clays in each stack, $d_S =$ Thickness of nano-clay, $d_P =$ Thickness of effective particle=$d_s+2d_i+(N-1)d_{(001)}$ with $d_{(001)}$ as average interlayer space considered as 4.1 nm. The aspect ratio of effective particle a =d_p/l with l as the length of nanoclay platelet. In the second step, the overall longitudinal modulus of the two phase composite (effective particle+polymer) is obtained by **Mori-Tanaka** model as follows.

$$E = \frac{\{(A_{11} + A_{22} + A_{32})V_p V_m + [A_{11}(A_{22} + A_{32}) - 2A_{12}A_{21}]V_m{}^2 + V_p{}^2\}}{\{V_p V_m[2A_{21}(S_{12}{}^m - S_{12}{}^p) + (A_{22} + A_{32})S_{11}{}^p + A_{11}S_{11}{}^m] + [A_{11}(A_{22} + A_{32}) - 2A_{12}A_{21}]S_{11}{}^m V_m{}^2 + S_{11}{}^p V_p{}^2\}} \tag{12}$$

Where,

$$\begin{aligned} S_{11} &= 1/E_{11} \\ S_{12} &= -(\upsilon_{12}/E_{11}) \end{aligned} \tag{13}$$

$$A_{11} = \frac{E^m}{E_{11}{}^p}\left[1 + \frac{\upsilon^m(\upsilon^m - \upsilon_{12}{}^p)}{(1+\upsilon^m)(1-\upsilon^m)}\right] \tag{14}$$

$$A_{12} = \frac{E^m \upsilon^m (1-\upsilon_{12}{}^p)}{E_{22}{}^p 2(1+\upsilon^m)(1-\upsilon^m)} - \frac{E^m \upsilon_{12}{}^p}{E_{11}{}^p (1+\upsilon^m)(1-\upsilon^m)} + \frac{\upsilon^m}{2(1-\upsilon^m)} \tag{15}$$

$$A_{21} = \frac{E^m(\upsilon^m - \upsilon_{12}{}^p)}{E_{11}{}^p 2(1+\upsilon^m)(1-\upsilon^m)} \tag{16}$$

$$A_{22} = \frac{E^m(\upsilon_{12}{}^p - 3)}{E_{22}{}^p 8(\upsilon^m - 1)(\upsilon^m + 1)} + \frac{E^m \upsilon_{12}{}^p \upsilon^m}{E_{11}{}^p 2(\upsilon^m - 1)(\upsilon^m + 1)} + \frac{(\upsilon^m + 1)(4\upsilon^m - 5)}{8(\upsilon^m - 1)(\upsilon^m + 1)} \tag{17}$$

$$A_{32} = \frac{E^m(3\upsilon_{12}{}^p - 1)}{E_{22}{}^p 8(\upsilon^m - 1)(\upsilon^m + 1)} + \frac{E^m \upsilon_{12}{}^p \upsilon^m}{E_{11}{}^p 2(\upsilon^m - 1)(\upsilon^m + 1)} + \frac{(\upsilon^m + 1)(1 - 4\upsilon^m)}{8(\upsilon^m - 1)(\upsilon^m + 1)} \tag{18}$$

Here E and G are elastic and shear modulus of a nanocomposite material, respectively, υ is a Poisson's ratio and V_p, V_m are the volume fraction of particle and matrix in nanocomposite. Also the volume fraction of nanoclay in the composite is given in terms of weight fraction according to the following equation:

$$V_s = \frac{\rho_m}{\rho_s}\frac{w_s}{\Psi} \tag{19}$$

$$\Psi = \frac{1}{\left(1-\frac{1}{N}\right)\left(\frac{d_{(001)}}{d_s}\right)+\frac{1}{N}} \tag{20}$$

Where w_s are the weight fraction of nano-clay platelets, ρ is the density of materials. A density of matrix ρm = 1000 kg m^{-3}. The density of nano-clay platelets are 3067 kg m^{-3}.

The **Halpin-Tsai** model to predict the effective properties of nanocomposite as follows,

$$\frac{E}{E_m} = \frac{1+(\varepsilon\eta V_p)}{1-(\eta V_p)} \tag{21}$$

$$\eta = \frac{(E_P / E_m)-1}{(E_P / E_m)+\varepsilon} \tag{22}$$

Where, E is the elastic property of hybrid composite and E_m is elastic properties of polymer matrix. ε is the measure of reinforcement of the composite and it depends upon geometry of fiber. For longitudinal modulus of elasticity $\varepsilon = 2l/d_p$ and for transverse modulus of elasticity $\varepsilon = \sqrt{3}\log(l/d_p)$ of rectangular fiber geometry. E_P and V_p is the elastic property and volume fraction of effective particle in the nanocomposite.

3.1.2 Thermal properties

Fiber reinforced polymer nanocomposite shows excellent thermal characteristics like thermal resistance and thermal expansion. For this analysis many theoretical models are available to predict the thermal conductivity of nanocomposite, the simplest of these are rule of mixture. There are three types of rule of mixture series, parallel, geometric.

Series model, $K_C = (1-V_p)K_m + V_p K_p$ (23)

Parallel model, $K_C = \frac{(1-V_p)}{K_m} + \frac{V_p}{K_p}$ (24)

Geometric model, $K_C = K_m^{(1-V_P)} K_p^{V_P}$ (25)

Here the series model overestimate the value so it set the upper limit and parallel model underestimate the value so it set the lower limit of properties so modified these rule by Halpin-Tsai model.

Rule of mixture for obtaining the value of thermal conductivity of effective particle as

$$K_P = (1-\alpha)K_I + \alpha K_f \tag{26}$$

Thermal properties of nanocomposite is obtained by the Halpin-Tsai model are as follows,

$$\frac{K_C}{K_m} = \frac{1+\varepsilon\eta V_p}{1-\eta V_p} \tag{27}$$

Where,

$$\eta = \frac{(K_P / K_m) - 1}{(K_P / K_m) + \varepsilon} \tag{28}$$

For this the value of geometry factor $\varepsilon = 1$, K_f indicates thermal conductivity of clay fiber and K_P, K_m is the thermal conductivity of particle and the polymer matrix respectively and the K_C represents the thermal conductivity of nanocomposite.

3.2 Modeling of Hybrid composite

To obtain the elastic properties of three phase polymer composite, Halpin-Tsai model and theory of micromechanics were applied. The rule of mixture is used to obtain the effective elastic modulus of effective clay particle and effective CNT particle.

$$E_{CP} = E_{clay}\alpha + E_{\text{int}}(1-\alpha) \tag{29}$$

$$E_{CF} = E_{cnt}\phi + E_{\text{int}}(1-\phi) \tag{30}$$

Where E_{CP} and E_{CF} are the effective elastic modulus of clay particle and CNT particle. E_{clay}, E_{cnt}, α, ϕ are the elastic modulus and volume fractions of clay and CNT respectively.

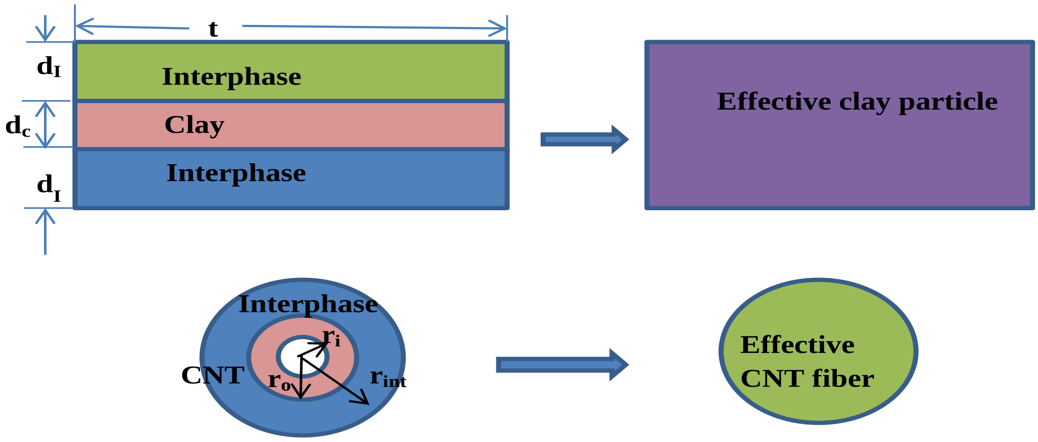

Fig.3.1 Representation of effective Clay particle and effective CNT fiber

To obtain the effective elastic modulus of hybrid composite by combining effective particle and polymer (epoxy) by using modified Halpin-Tsai model as follow.

$$\frac{P}{P_m} = \frac{1+(\varepsilon_1\eta_{CP}V_{CP} + \varepsilon_2\eta_{CF}V_{CF})}{1-(\eta_{CP}V_{CP} + \eta_{CF}V_{CF})} \tag{31}$$

Where, P is the elastic property of hybrid composite and Pm is elastic properties of polymer matrix.

$$\eta_{CP} = \frac{(E_{CP}/E_m)-1}{(E_{CP}/E_m)+\varepsilon_1} \tag{32}$$

$$\eta_{CF} = \frac{(E_{CF}/E_m)-1}{(E_{CF}/E_m)+\varepsilon_2} \tag{33}$$

$$V_m + V_{CP} + V_{CF} = 1 \tag{34}$$

For, longitudinal elastic modulus $\varepsilon_1 = (2l/dp)$ $\varepsilon_2 = (2l/t)$, and for transverse elastic modulus $\varepsilon_1 = \sqrt{3}\log\,(l/dp)$ and $\varepsilon_2 = 1$. Where $dp=dc+2*di$, total thickness of effective clay particle.

3.3 Numerical modeling of clay/polymer nanocomposite

3.3.1 Aligned fiber 3D RVE

The model is considered as homogeneous elastic polymer filled with isotropic filler material. All the computations are performed on a Representative Volume Element (RVE) of cylindrical cross-section. In order to specify the morphology, it is assumed that the matrix is continuous in length in the form of solid cylinder and perfectly aligned .The coupling between matrix and fiber is simulated with an interfacial region. The dimensions of RVE are defined according to the desired volume fraction. The analysis is conducted using 3D finite element model of RVE developed in commercial ANSYS software. Higher order 3D SOLID 45 brick elements are used to represent all the constituents. An optimum element size (mesh density) that leads to a fully converged Solution with minimum computational time is determined based on parametric study. In order to predict elastic moduli, the RVE is loaded in axial tension by applying a small normal displacement at one side and fully restraining the other side. The periodic boundary condition applied for analysis and axial displacement is given at (z=0) and it fixed at (z=L). The strain and stress are calculated at the fixed end and it employed to evaluate the effective elastic properties of nanocomposite. Fig.3.2 shows the modeling of 3D RVE for stress analysis on ANSYS by considering solid 45 element with specific elastic properties of matrix, fiber and interface material to obtained the longitudinal effective elastic modulus of nanocomposite material. In this analysis we obtained the stress at fixed end by providing the axial displacement (10nm) at other end.

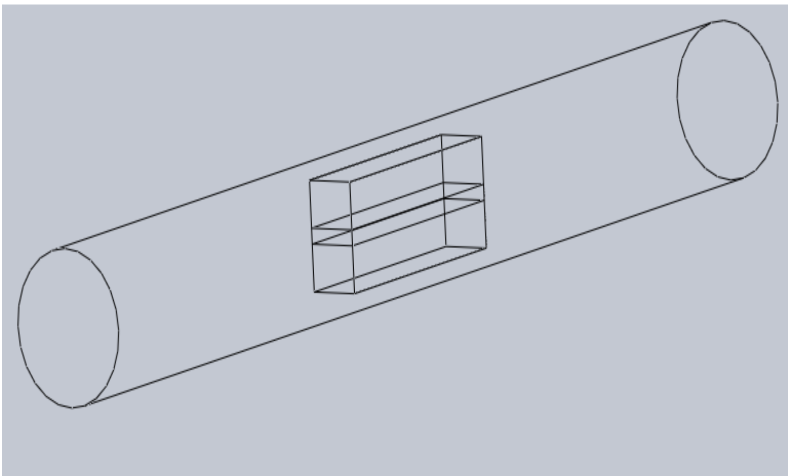

Fig 3.2 Modeling of aligned fiber 3D RVE

We know stress and strain relationship is $\sigma = E_c \varepsilon$, where σ is total stress on fixed end of nanocomposite and ε is the total mechanical strain in longitudinal direction and E_C is the longitudinal effective elastic modulus of nanocomposite.

3.3.2 Random orientated fiber 2D RVE

A 2D representative volume element (RVE) constructed on the Ansys Apdl 15.0 to analyse the mechanical properties of randomly oriented fiber reinforced polymer nanocomposite. The randomly distributed fiber is generated by Boolean operation. A periodic boundary condition applied to the RVE and it meshed with plane182 element type, one end fixed and give some displacement at the opposite end and evaluate the stress and strain at fixed end and evaluate the effective elastic modulus by simple Hook's law of elasticity.

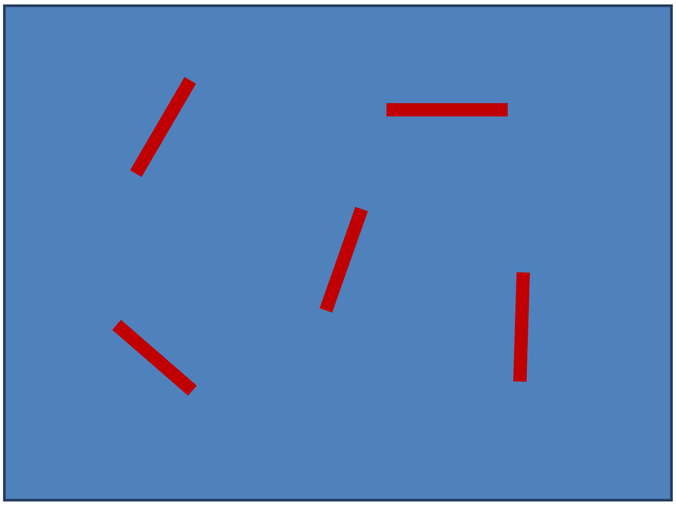

Fig. 3.3 Modeling Randomly oriented fiber 2D RVE

3.4 Numerical modeling of Hybrid composite

3.4.1Constitutive relations and RVE model

For a transversely isotropic composite, the material behavior is based on only five independent constants. This concept is particularly ensured for regular fiber arrangement. In this work arbitrary fiber distributions are considered which results in transversely isotropic properties. By considering effective stiffness coefficient and average stress-strain value, the constitutive equations for the homogenized composite can be expressed as

$$\begin{Bmatrix} \overline{\sigma_1} \\ \overline{\sigma_2} \\ \overline{\sigma_3} \\ \overline{\sigma_4} \\ \overline{\sigma_5} \\ \overline{\sigma_6} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{12} & C_{23} & C_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(C_{22} - C_{23}) & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{66} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \overline{\varepsilon_1} \\ \overline{\varepsilon_2} \\ \overline{\varepsilon_3} \\ \overline{\gamma_4} \\ \overline{\gamma_5} \\ \overline{\gamma_6} \end{Bmatrix} \tag{35}$$

A representative volume element model can be used for the calculation of effective elastic coefficients by applying the appropriate periodic boundary conditions under the assumption of periodicity of fiber arrangement. Figure 2 shows the RVE model for CNT-clay reinforced polymer composite.

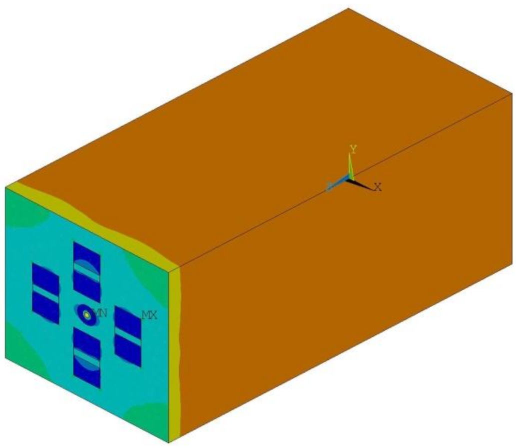

Fig. 3.4 RVE of CNT/clay reinforced polymer

The main advantage of the method is to replace the original composite with globally homogenized equivalent medium with same strain energy stored. To find out effective elastic coefficients such load cases with different boundary conditions must be applied that for a particular load case only one value in the strain field vector is non-zero and all other becomes zero. Then from corresponding column, the effective coefficients can be determined using calculated average stress value corresponding to unit strain.

3.4.2 Finite element modeling

A three dimensional multi-field elements is used for finite element calculations using FE package ANSYS. ANSYS Parametric Design Language (APDL) coding is used for modeling and applying the constraint equations. An algorithm was written in APDL for automated generation of RVE with aligns CNT and clay inside the polymer matrix. First 2-D model is generated in X_2-X_3 plane with circle as CNT and rectangle as clay and meshed with PLANE82 element. Further FE mesh is extruded in X_1 direction with SOLID185 3-D element for meshing of RVE. Fibers surfaces are connected by Boolean operation with the aim of predicting the modulus of resin matrix reinforced with periodic nano-reinforcement of clay-CNTs. An interphase region is also considered here between CNT/polymer and clay/polymer to demonstrate the imperfect load transfer phenomenon at interfaces. The interphase region is meshed with random material properties lies between fiber and polymer matric properties. The generation of RVE can be controlled by some input parameters like size of RVE, CNT and clay diameters for desired volume fraction. A certain minimum distance must be ensuring to generate suitable meshing of each part of model. From the numerical analysis, the effective elastic parameters of compositional material were estimated by relating boundary conditions. In order to evaluate the overall stiffness matrix [C] of hybrid composite, the RVE is subjected to an average strain. The six components of strain are applied by imposing the following boundary conditions on the displacement components.

$$u_i(a_1, x_2, x_3) - u_i(-a_1, x_2, x_3) = 2a_1\varepsilon_{i1} \qquad \begin{array}{l} -a_2 \le x_2 \le a_2 \\ -a_3 \le x_3 \le a_3 \end{array}$$

$$u_i(x_1, a_2, x_3) - u_i(x_1, -a_2, x_3) = 2a_2\varepsilon_{i2} \qquad \begin{array}{l} -a_1 \le x_1 \le a_1 \\ -a_3 \le x_3 \le a_3 \end{array}$$

$$u_i(x_1, x_2, a_3) - u_i(x_1, x_2, -a_3) = 2a_3\varepsilon_{i3} \qquad \begin{array}{l} -a_1 \le x_1 \le a_1 \\ -a_2 \le x_2 \le a_2 \end{array} \tag{36}$$

Here $2a_j\varepsilon_{ij}$ represents the applied displacement necessary to enforce a strain ε_{ij} over a distance $2a_j$. The strain applied on boundary results in complex state of strain inside the RVE. So, volume average strain in the RVE equals to the applied strain, i.e.

$$\overline{\varepsilon_{ij}} = \frac{1}{V}\int_V \varepsilon_{ij}\, dV = \varepsilon_{ij} \tag{37}$$

Considering hybrid composite as homogeneous material, the average stress-strain relationship can be written as

$$\overline{\sigma_\alpha} = C_{\alpha\beta}\overline{\varepsilon_\beta} \tag{38}$$

By choosing a unit applied strain in one direction and imposing periodic boundary conditions on other directions, stress field can be computed. Whose average value over the volume gives the required components of stiffness matrix, one column at a time.

$$C_{\alpha\beta} = \overline{\sigma_{\alpha}} = \frac{1}{V}\int_{V} \sigma_{\alpha}(x_1, x_2, x_3) dV \tag{39}$$

Where α, β are varying 1 to 3. Gauss-Legendre quadrature can be used for evaluating the volume integrals of a finite element. Commercial ANSYS have such type of capability to evaluate the average stress over the volume, element by element. Three loading cases are imposed to evaluate the all elastic coefficient of [C] for isotropic composite. Figure 3.5 (a, b) shows the meshing of RVEs used in finite element analysis. Fig.3.5 (a) shows the meshing of RVE with variation clay particle i.e. the volume fraction of effective clay particle is increasing with increasing the effective clay particle into the RVE model where as the CNT volume fraction is keeping constant. But in Fig. 3.5 (b) the CNT effective particle volume fraction is increasing while clay particle volume fraction keeping constant.

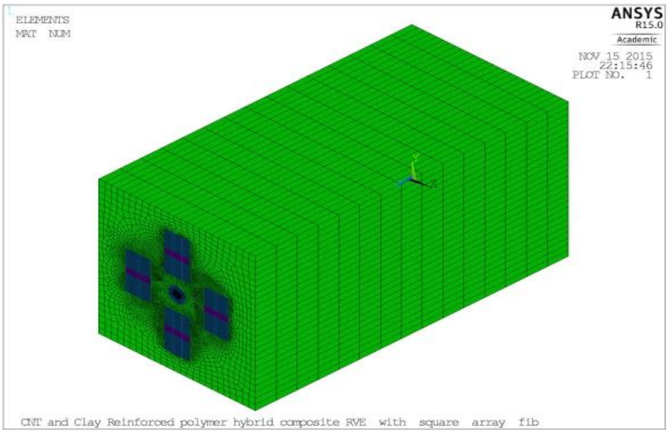

Fig 3.5 (a) Meshing of square RVE with variation of clay platelets

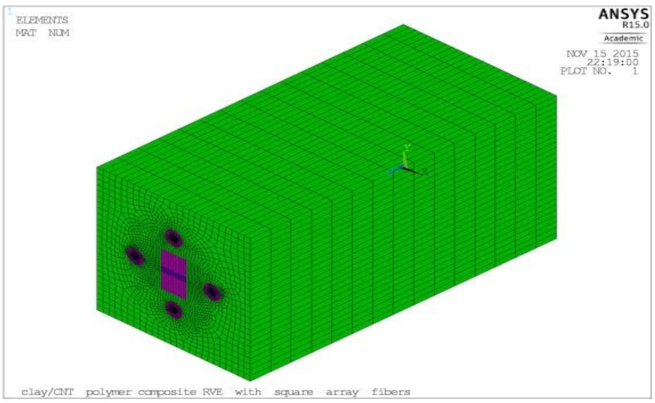

Fig. 3.5 (b) Meshing of square RVE with variation of CNT fiber

Chapter 4

Results and discussion

This chapter presents the numerical results of nanoclay/polymer and hybrid composite whose properties are considered from references.

4.1 Nanoclay reinforced polymer composite

Heterogeneous materials such as composites consist of clearly different phases that show different material properties. A homogenization task performed to evaluating the response of nanocomposite by combining the properties of individual constituents. To rely on micromechanical modeling the micromechanical modeling theory must be validated with the experimental data or finite element model.

Based on the micromechanical formulations a program is developed in MATLAB, with following data considered for exfoliated morphology. Table 4.1 shows the material elastic properties with two case of interphase properties considered for this analysis.

Table 4.1 Elastic data for exfoliated morphology composite

Material		Elastic Modulus (GPa)	Poisson ratio	Thickness (nm)
Matrix(Nylon-6)		2.8	0.35	-
Nanoclay (MMT)		178	0.28	1
Interphase	(I)	13	0.35	3
	(II)	2.8	.35	3

By using these properties, of different phases of nanocomposite in the Table 4.1 the mechanical properties are computed. Based on the micro-mechanical model effective elastic properties of nano-clay reinforced polymer composites are computed and effects of weight fraction, aspect ratio, volume fraction and stacks of nanoclay on effective elastic behavior of composite is illustrated.

Fig4.1 shows the non-dimensional stiffness (E_C/E_M) value of nanocomposite is increasing with weight fraction of nanoclay in composite i.e. increasing the weight fraction of nanoclay in the composite make stiffer to the component. There is linear variation seen.

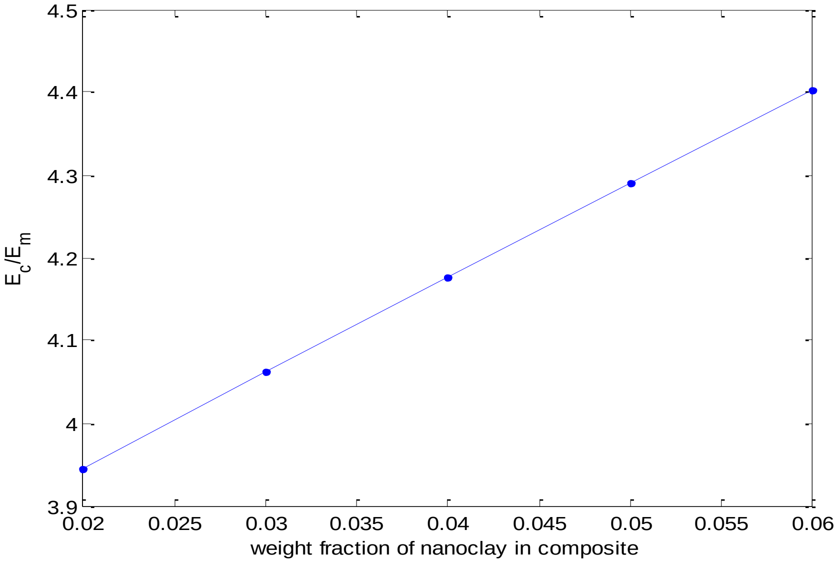

Fig 4.1Variation of non-dimensional stiffness with weight fraction of nanoclay

In Fig. 4.2, elastic modulus is plotted against number of stacks of nanoclay platelets, stacks include one nanoclay platelet and surrounded by two intephase. It seems that elastic modulus   is increases slowly upto 4 stacks and rises thereafter drastically due to difference of slopes.

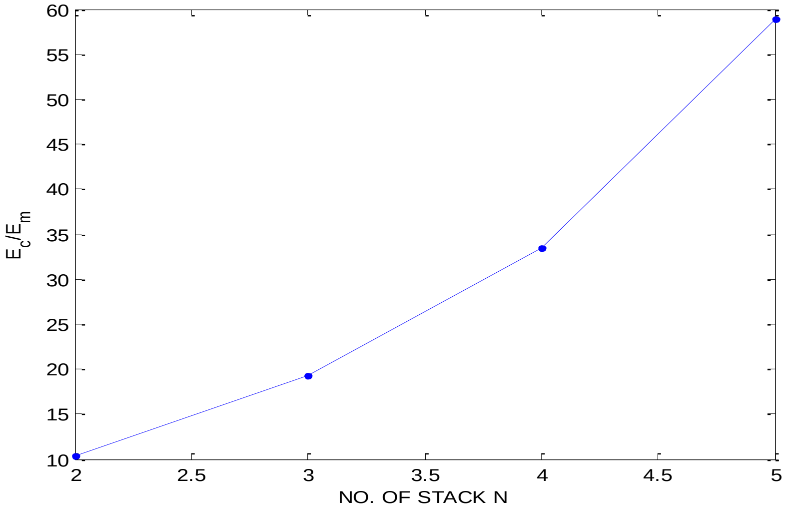

Fig 4.2 Variation of non-dimensional stiffness with no.of stacks in the nanocomposite

In fig.4.3 the variation of effective elastic properties of nanocomposite with respect of aspect ratio is presented, it can be seen that the variation is non-linear. Aspect ratio gives more impact on the modulus of nanocomposite.

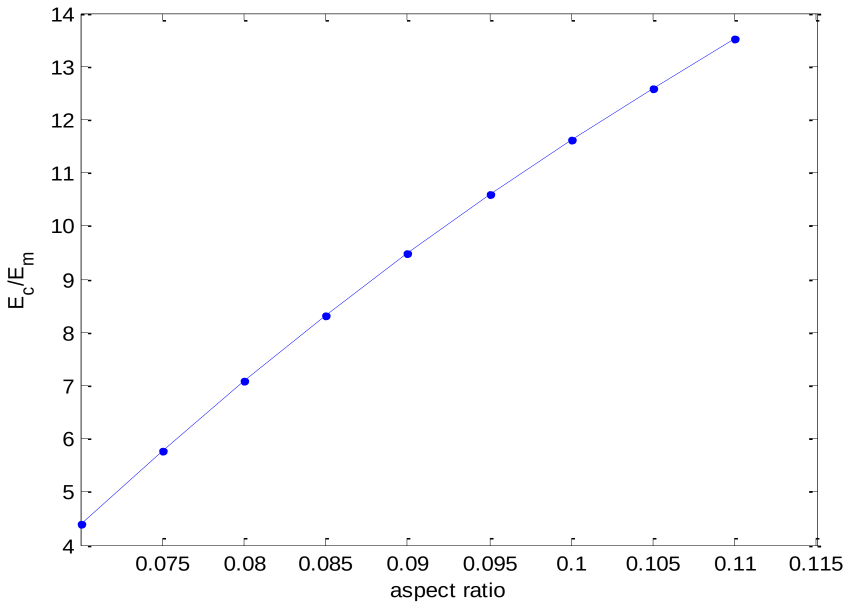

Fig. 4.3 Variation of non-dimensional stiffness with aspect ratio of nanoclay

In fig.4.4 the effective elastic modulus is varies with the volume fraction of nanoclay in the composite with variation of stacks of nanoclay, it can be seen that the variation is linear and value of effective elastic modulus increasing with increasing the volume fraction as well as with no. of stacks.

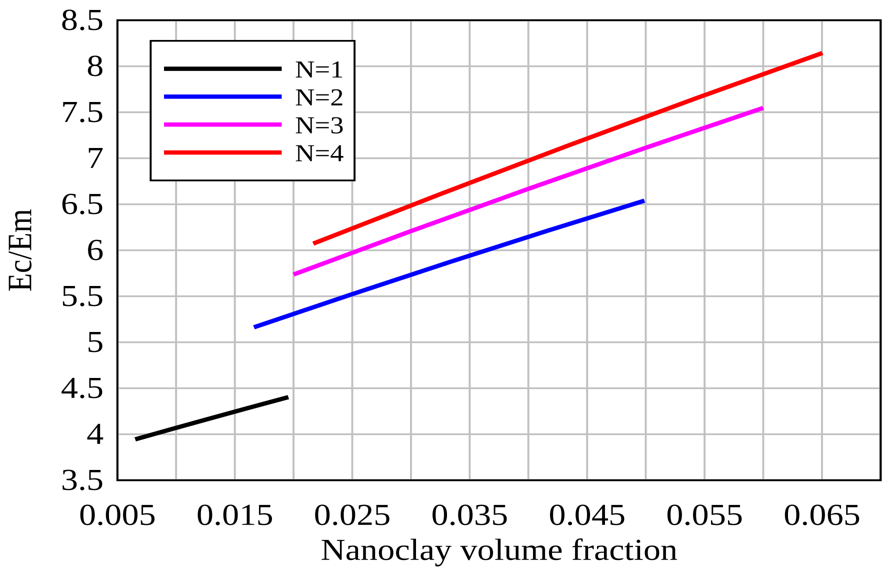

Fig. 4.4 Variation of non-dimentional stiffness with nanoclay volume fraction

In fig.4.5 shows the variation of effective elastic properties of nanocomposite with the taking the interphase properties of exfoliated morphology of second case in Table1 with variation of volume fraction of nanaoclay in composite. It can be seen from figure the effective elastic properties of nanocomposite increases with no. of stacks.

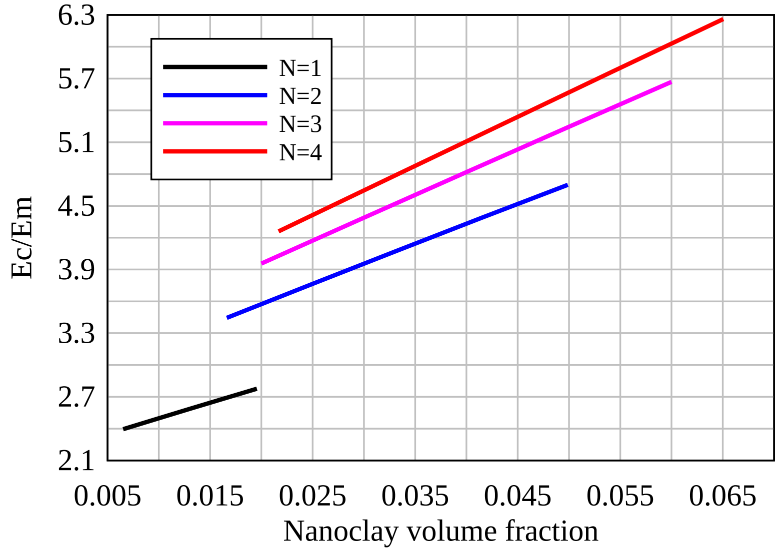

Fig.4.5 Variation of non-dimensional stiffness with nanoclay volume fraction.

Fig. 4.6 shows the variation of effective elastic properties of nanocomposite in comparison of polymer matrix modulus is increasing with increasing the value of weight fraction of nanoclay.

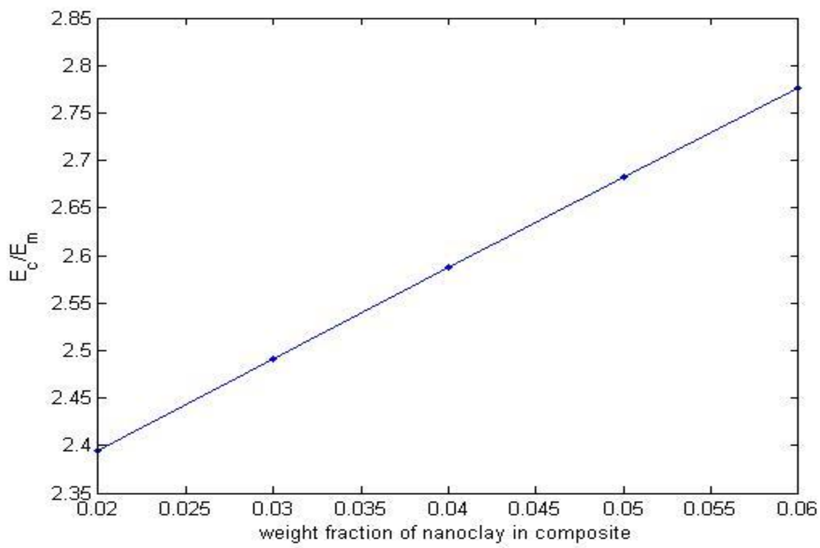

Fig.4.6 Variation of non-dimensional stiffness with variation of weight fraction of nanoclay.

In fig.4.7 shows the analysis on ANSYS APDL 15.0 with the periodic boundary conditions and fixed one end and give displacement at other end and taken the average value of stress and atrain and obtain the effective elastic modulus.

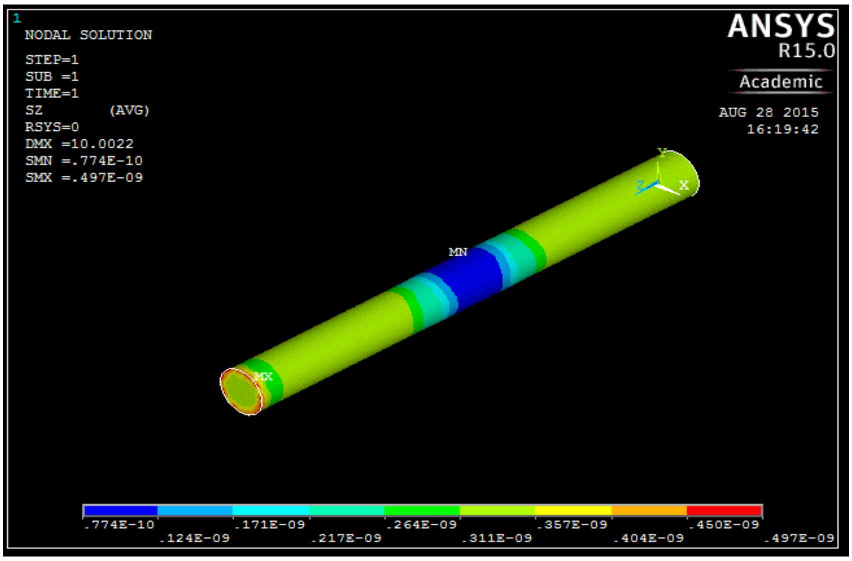

Fig.4.7 Variation of stress of 3D RVE on Ansys of exfoliated morphology

We know stress and strain relationship is $\sigma = E_c \varepsilon$, where σ is total stress on fixed end of nanocomposite and ε is the total mechanical strain in longitudinal direction and E_C is the longitudinal effective elastic modulus of nanocomposite.The elastic modulus of composite obtained from ansys solution corresponding to a volume fraction is 4.127 GPa.

Table4.2 shows the properties of different phases of constituents of nanocomposite for intercalated morphology. By using this property we can found the effective elastic properties of nanocomposite.

Table 4.2 Elastic data for intercalated morphology composite

Material	Elastic modulus (GPa)	Poisson ratio	Thickness (nm)
Matrix MXD6 (Nylon)	4.14	0.35	-
Nanoclay (MMT)	178	0.28	1
Gallery	4.14	0.35	3.1

Fig.4.8 shows the variation of effective elastic properties of intercalated morphology with variation of volume fraction of stacks in the particle. The result of micromechanical model is slightly more than the finite element analysis. Intercalated morphology shows less effective elastic properties than the exfoliated morphology.

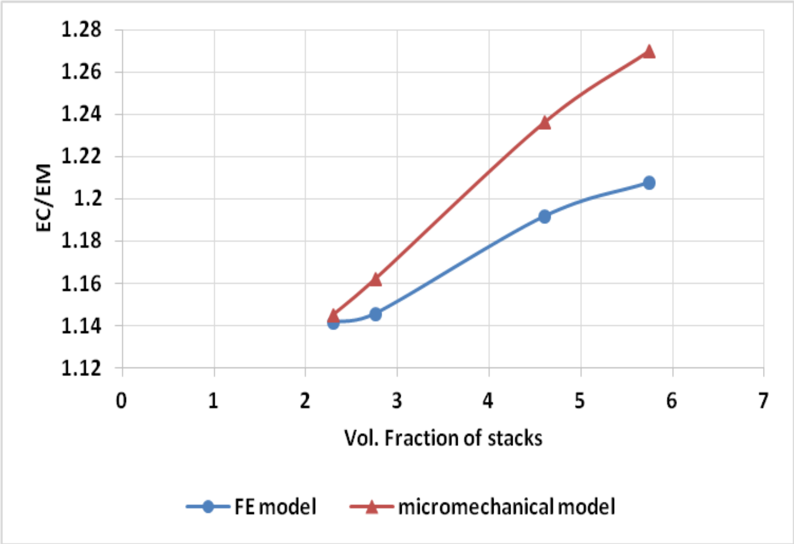

Fig.4.8 Variation of non-dimensional stiffness with variation of volume fraction of stacks

Fig.4.9 shows the analysis of 2D RVE with randomly oriented and distributed on ANSYS APDL15.0, the figure shows the variation of stress along the length of square RVE. The results are obtained by taken the average value of stress and strain.

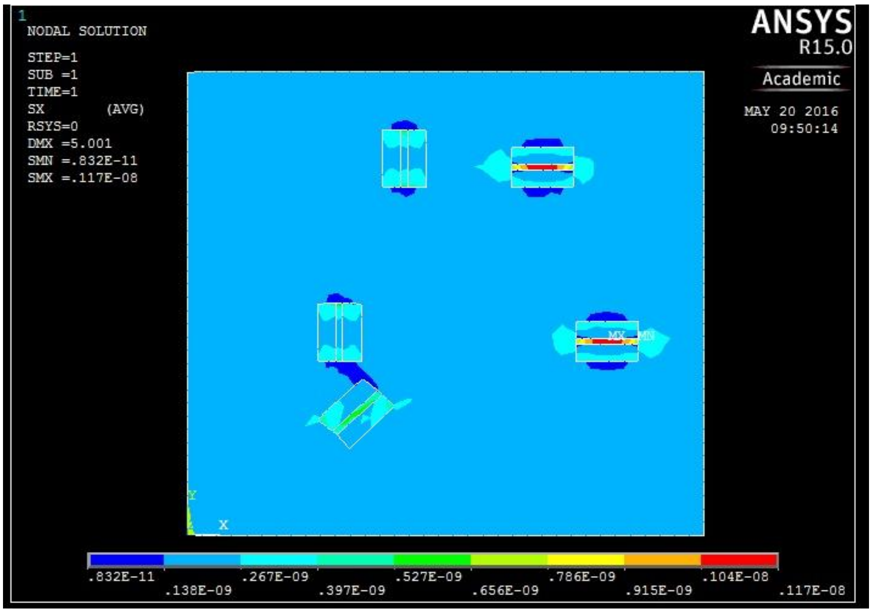

Fig.4.9 Variation of stress of 2D RVE on ANSYS for random orientation.

Fig.4.10 shows the variation of effective elastic modulus with respect of effective particle volume fraction in the composite. The variation shows linear of non-dimensional stiffness with volume fraction of effective particle. 2D RVE is not more effective than the 3D RVE, the more effective and efficient result come by analysis 3D RVE of nanocomposite.

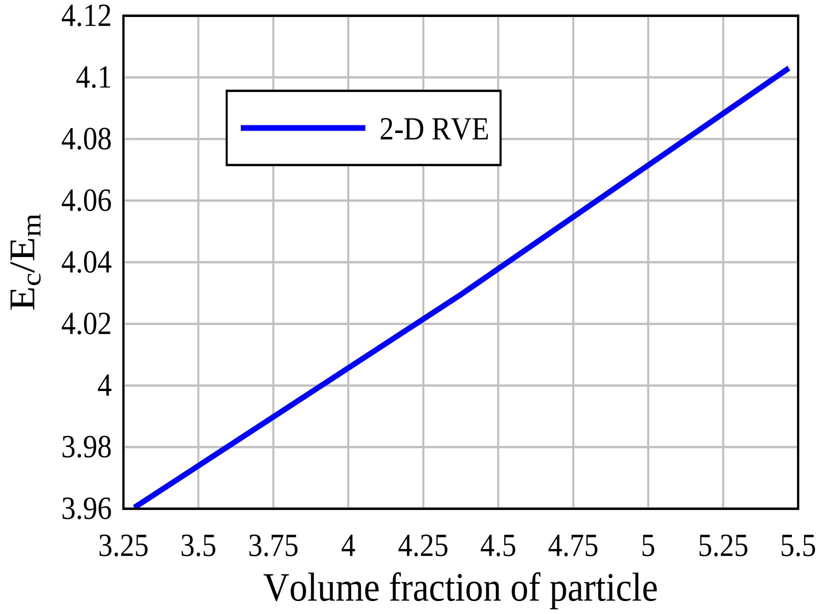

Fig.4.10 Variation of non-dimensional stiffness with effective particle volume fraction

By watching the behaviour of elastic modulus with weight fraction, number of stacks,aspect ratio and nanoclay volume fraction, it is planned to formulate an optimum design problem by selecting the best values of weight fraction, aspect ratio and nanoclay volume fraction that maximizes the elastic modulus.

4.2 Thermal conductivity of clay reinforced polymer nanocomposite

The results are obtained by the using micromechanical modeling of nanocomposite, here Halpin-Tsai model is proposed to evaluate the Thermal conductivity of clay reinforced polymer nanocomposite.The following values of thermal conductivity of nanoclay and polymer are considered; k_f = 1.11w/m-k , km= 0.25w/m-k .

The Fig.4.11 shows the variation of effective thermal conductivity of exfoliated morphology of nanocomposite with respect to the volume fraction of particle in nanocomposite for different value of thermal conductivity of interphase. From figure it can be seen that the non-dimensional thermal conductivity of nanocomposite varies linearly with the volume fraction of effective particle. The thermal conductivity of clay and polymer matrix is very small so the figure shows very less value of thermal conductivity ratio for nanocomposite.

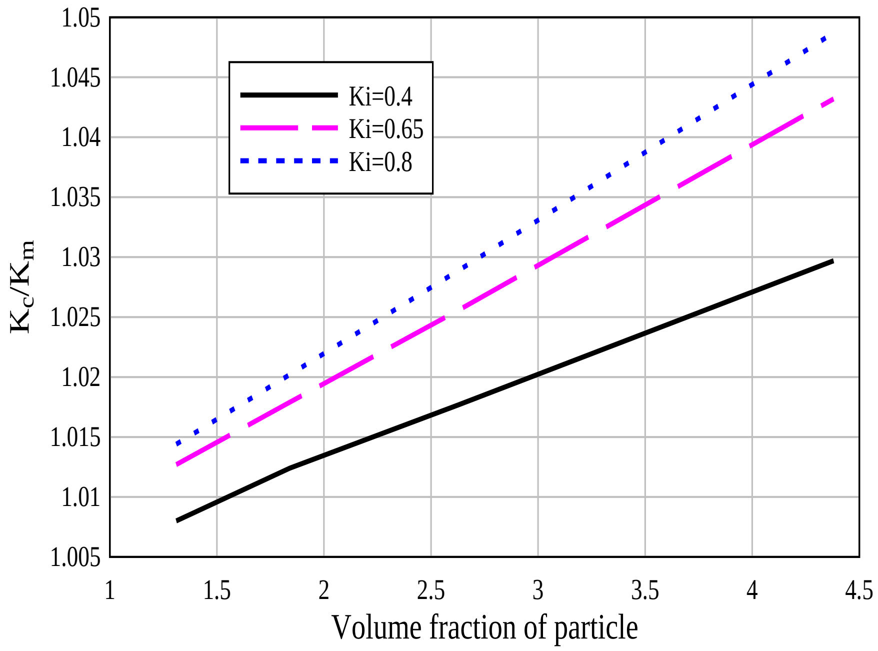

Fig.4.11 Variation of non-dimensional thermal conductivity with volume fraction of particle

4.3 Hybrid composite

The elastic behavior of polymer matrix reinforced by CNTs and nanoclay platelets is analyzed by considering interphase parameters. The advantages of nanoclay in CNT reinforced polymer composite can be explained with reduction of interfacial reinforcing area of CNTs and enhancing the interfacial adhesion and dispersion of CNTs in polymer matrix. The effective elastic and geometric properties of each phase of RVE is given in Table 4.3. For ease of calculation RVE length is considered as 50 nm. The table shows the properties of nanoclay, CNT and epoxy polymer matrix and for this work the interphase value or properties taken as constant and equal, this will make calculation more easy and simple in micromechanical modeling. Using of these properties of each phase of hybrid composite given in the table below, analysis of hybrid composite is done by finite element method or numerical modeling and by micromechanical modeling. The average value of stress and strain is obtained then calculates the effective elastic modulus of hybrid composite.

Table 4.3 Material properties of all phases in RVE for hybrid composite

Material	Elastic Modulus (Gpa)	Poisson's ratio (μ)	Geometry
Epoxy	2.026	0.4	25x25 nm
CNT	1054	0.25	r_i=0.315nm, r_o=0.650nm
Clay (MMT)	178	0.28	t=4 nm, d_c=1 nm
CNT/polymer interphase	16.10	0.4	r_{int}=1.404 nm
Clay/polymer interphase	16.10	0.4	d_I=3 nm

Fig.4.12 shows the stress varies along the length of the square RVE, the maximum stress at the fixed end condition and the effective elastic properties calculated with the taking average value of stress. The displacement given along the z-axis and the particle is aligned along the same axis so the stress is longitudinal stress presented in this figure.

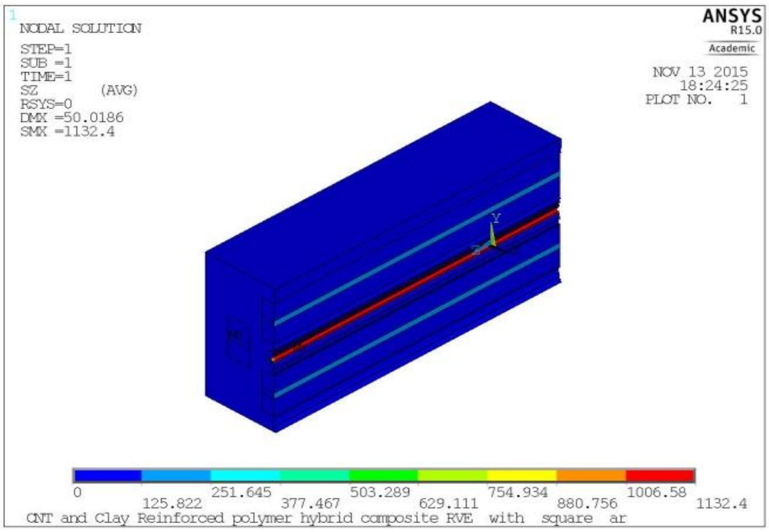

Fig.4.12 Variation of stress

Fig.4.13 shows the strain along the length of RVE or along z-axis, the starin taken for obtaining the effective value of elastic properties is average value.

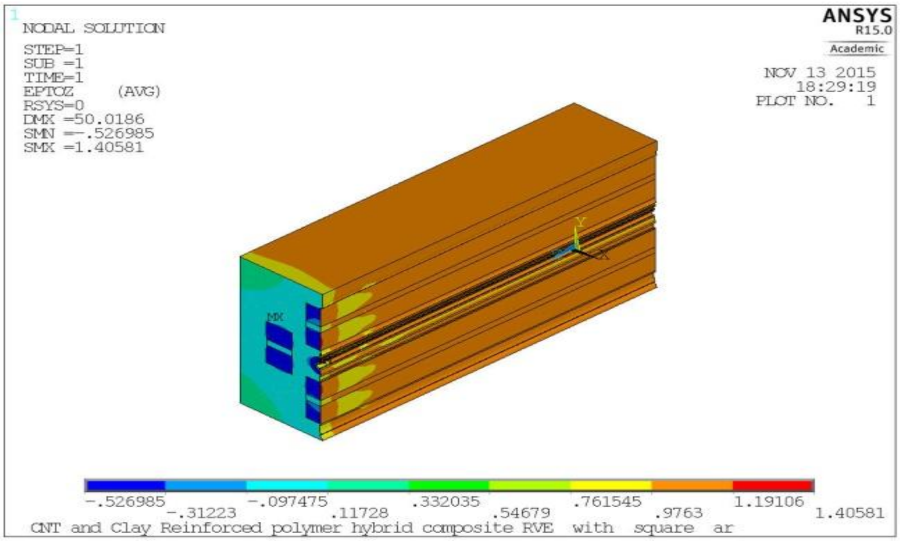

Fig 4.13 Variation of strain

A case study has been illustrated to reveal the importance of nano-clay reinforcement in CNT reinforced composite. Table 4.4 shows the elastic properties of CNT/clay hybrid composite considering four types of RVE i.e. the variation of clay platelets with constant volume fraction of CNT. The finite element modeling results are validated with micromechanical modeling results. In Table 4.5 elastic moduli are investigated considering constant volume fraction of clay platelets inside hybrid composite. It can be concluded from predicted results, four CNT with one clay based RVE gives better results as compared to one CNT with four clay RVE.

Table 4.4 Elastic properties of hybrid composite with variation of Number of clay platelets

RVE with	E_L	E_T	G_T	υ_L	υ_T
1 CNT	3.667	2.2119	0.738	0.395	0.5054
1 CNT +1 Clay	5.3245	2.420	0.7868	0.3938	0.5382
1 CNT + 2 Clay	7.0019	2.626	0.8468	0.3938	0.5508
1 CNT + 3 Clay	8.6448	2.8338	0.9092	0.3928	0.5582
1 CNT +4 Clay	10.2846	3.0908	0.9929	0.3917	0.5564
Micromechanics modelling	9.8932	2.9931	0.9865	0.3899	0.5423

In Table 4.5 elastic moduli are investigated considering constant volume fraction of clay platelet inside hybrid composite.

Table 4.5 Elastic properties of hybrid composite with variation of Number of CNTs

RVE with	E_L	E_T	G_T	υ_L	υ_T
1 Clay	3.6576	2.3079	0.7719	0.3952	0.4949
1 Clay +1 CNT	5.3236	2.4137	0.7838	0.3948	0.5397
1 Clay + 2 CNT	6.9921	2.4899	0.7963	0.3944	0.5634
1 Clay + 3 CNT	8.6552	2.5700	0.8164	0.3940	0.5753
1 Clay +4 CNT	10.3201	2.6521	0.8381	0.3935	0.5820

The above table shows the longitudinal, transverse and shear modulus also the passions ratio along the longitudinal and transverse direction. It can be seen that the shear modulus and transverse modulus mostly increases with the increasing the volume fraction of nanoclay platelets and CNT fiber in the hybrid composite. A nano structured hybrid composite composed of clay nano particle and carbon nanotubes are studied using finite element modeling. RVE model constructed to demonstrate the exact composite structure up to some extent. Predicted values from FE modeling are compared with corrected Halpin-Tsai model. Results are comparable and elastic modulus of RVE model is much closer micromechanics based results.

Fig.4.14 shows the variation of non dimensional stiffness with volume fraction of nanoclay, keeping the CNT volume fraction constant using modified form of Halpin –Tsai model.

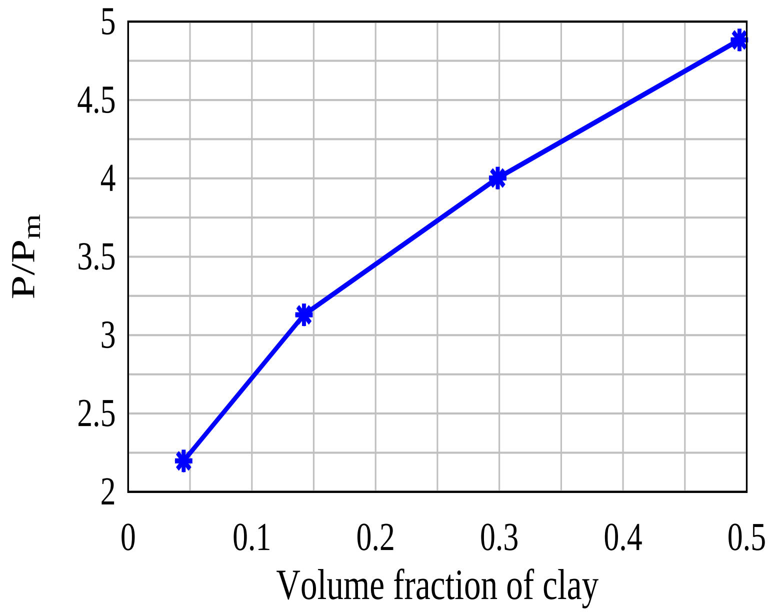

Fig.4.14 Variation of nondimensional stiffness with volume fraction of nanoclay

Fig.4.15 shows the variation of elastic behavior of hybrid composite with variation of volume fraction of CNT keeping the volume fraction of nanoclay platelets constant . In the Fig. 4.15 P is the elastic modulus of hybrid composite and P_m denotes the modulus of elasticity of polymer matrix. This results are obtain by the modified Halpin-Tsai model of hybrid composite with varrying CNT volume fraction.

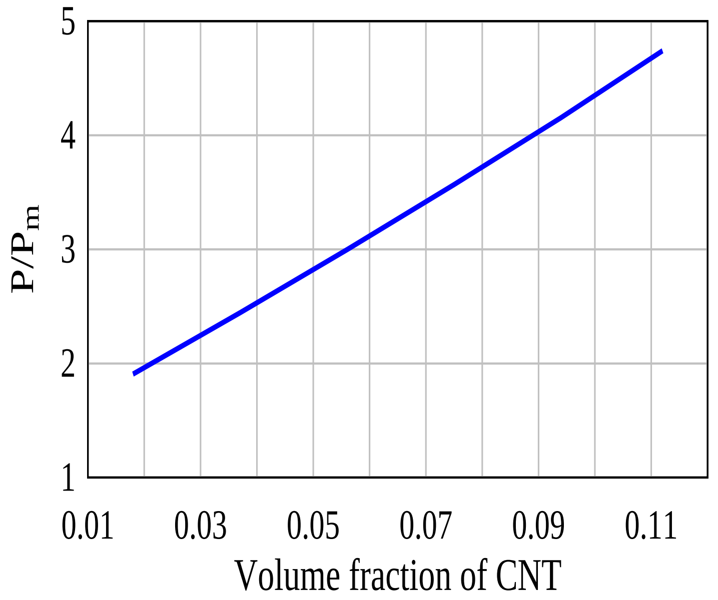

Fig.4.15 Variation of non-dimensional stiffness with volume fraction of CNT

4.4 Experimental Analysis

This section explains briefly the basic experimental study carried out in this work

4.4.1 Preparation of nanocomposite

Firstly, 100gm of epoxy and 34 gm of hardener supplied by United nanotech innovations pvt. Ltd. Bangalore has been taken in the jar separately. Then the hardener is mixed with epoxy using magnetic stirrer technique for 5 minutes. After this mixing, 5gm of nanoclay particles are mixed with epoxy-hardener gel and hand stirring was carried out for 30 minutes. The whole sample poured into a rectangular mould prepared using two aluminium alloy plates and to remove the air bubbles from the mixture, it is placed in vacuum chamber for 10 minutes at moderate pressure. After that it cures for next 10 hours at room temperature to settle down. In this process, pure epoxy sample as well as epoxy with nanoclay is separately prepared using the same mould. Fig. 4.16 shows the mould which are used to prepared to make sample.

Fig.4.16 Mould to prepare sample

4.4.2 Preparation of test specimen

After the preparing of samples, they are cut into small pieces as specimens according to the requirement of test like tensile test and flexural test. These tests are conducted on the Instron testing machine available at metallurgy department. Fig. 4.17 shows the(a) pure epoxy and (b) nanoclay epoxy specimens.

(a)Epoxy specimen (b) Nanocomposite specimen

Fig.4.17 The test specimen prepared

4.4.3 Tensile test

Fig.4.18 shows the setup for tensile testing. Here the load is increased and a graph is plotted between deflection and load and finally stress-strain graph is obtained. Repeating three times an average value of the slope is taken as tensile modulus. The tensile modulus obtain for pure epoxy sample is 985.7 Mpa. Likewise, for the nanoclay epoxy sample the elastic modulus can be also found.

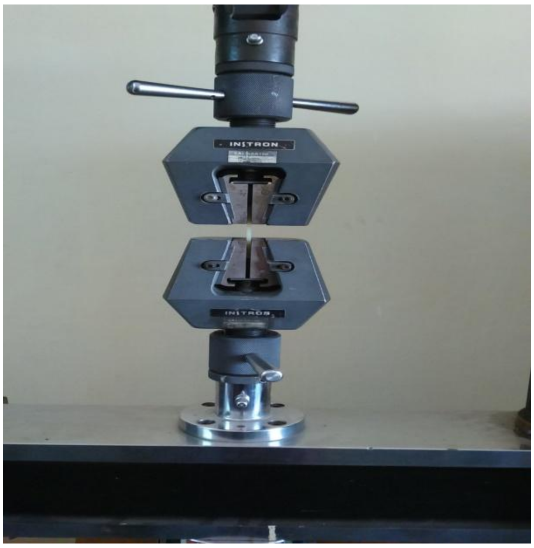

Fig.4.18 Tensile test setup

4.4.4 Flexural test

Fig. 4.19 shows the experimental setup for 3-point bending test. A flexural test specimen was prepared according to the ASTM D 638. Specimen size is prepared of the dimensions (80x10x4) mm, where the span length given between the supports is 64mm. The 3-point bending is performed to examine the flexural properties of the specimen on the Instron testing machine. The average value of flexure modulus is found to be 2.516 GPa for pure epoxy sample.

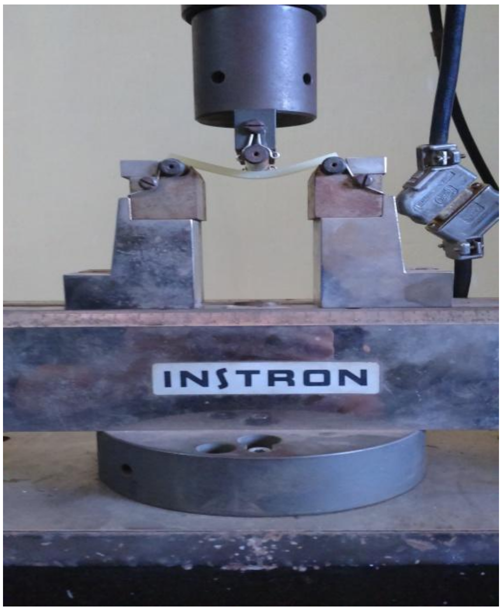

Fig.4.19 3-point bending test setup

Chapter 5

Conclusions

In this work, nanoclay polymer composite materials are exhaustively studied and their elastic modulus and thermal conductivity were predicted from the rule of mixtures, empirical methods and by using finite element modeling. Unlike graphene and CNT fibers, nanoclay platelets have interfaces always and it is required to first identify the properties of equivalent particle of nanoclay and interphase region. Following are the brief conclusion of present work.

- Three phase Halpin-Tsai model for elastic and thermal properties identification
- Studies on both exfoliated and intercalated morphologies with 2- step homogenization approach
- Use of 3D and 2D RVE concepts for finding the elastic constants of composite.

5.1 Future scope

Experimental analysis should be focused on the nanoclay content over the elastic properties along with rheological properties in a controlled atmosphere. Also the effects like nanoclay debonding on the overall properties have to be studied in more depth. The realization of effective properties of the hybrid composite should be verified with experiment.

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Appendix

Computer program for finding elastic properties of nanoclay polymer composite.

```
% find the value of youngs modulus of exfoliated morphology.
clc
close all
clear all
%numerical input
i=1;
for ws=.02:.01:.06
ES=178; % value in gpa
EI=13; % value in gpa
N=1;
nus=.28; % poission ratio of nano clay
nui=.35; % poission ratio of interphase
ds=1;% thickness of nano clay in nm
di=3;% thickness of interphase in nm
dp=ds+2*di;
l=10; %value of fibre length in nm
as=dp/l;
al=(ds/dp)*N;
E11=al*ES+(1-al)*EI;
BET=((nus^2*(EI/ES)+nui^2*((ES/EI)-2*nus*nui))/(al*ES+(1-al)*EI));
E22=((ES*EI)/(al*EI+(1-al)*ES-al*(1-al)*BET*EI*ES));
nu12=al*nui+(1-al)*nus;
nu13=((al*nus*ES*(1-nui^2)+(1-al)*nui*EI*(1-nus^2))/(al*ES*(1-nui^2)+(1-al)*nui*EI*(1-nus^2)));
GS=ES/(2*(1+nus));
GI=EI/(2*(1+nui));
eta=((nus^2*(GI/GS)+nui^2*((GS/GI)-2*nus*nui))/(al*GS+(1-al)*GI));
G12=(GS*GI)/(al*GI+(1-al)*GS-al*(1-al)*eta*GI*GS);
G13=E11/(2*(1+nu13));
%nano clay volume fraction in the composi
d00=4.1;
rm=1000;
```

```
rs=3067;
Vf=(rm/rs)*ws;
Vm=1-Vf;
%matrix data
Em=2.8;
num=0.35;
% mori tanka
S11m=1/Em;
S12m=(-num/Em);
S11f=1/E11;
S12f=(-nu12/E11);
A11=(Em/E11)*(1+(num*(num-nu12)/(1+num)*(1-num)));
A12=(Em/E22)*(num*((1-nu12)/(2*(1+num)*(1-num))))-((Em*nu12)/E11*(1+num)*(1-num))+(num/2*(1-num));
A21=(Em/E11)*((num-nu12)/(2*(1+num)*(1-num)));
A22=((Em/E22)*((nu12-3)/(8*(num-1)*(num+1))))+((Em/E11)*((nu12*num)/(2*(num-
        1)*(num+1))))+((num+1)*(4*num-5)/(8*(num-1)*(num+1)));
A32=((Em/E22)*((3*nu12-1)/(8*(num-1)*(num+1))))+((Em/E11)*((nu12*num)/(2*(num-
        1)*(num+1))))+((num+1)*(1-4*num)/(8*(num-1)*(num+1)));
E11C=((((A11+A22+A32)*Vf*Vm)+((A11*(A22+A32)-2*A12*A21)*Vf^2)+nu12^2)/(((Vf*Vm)*(2*A12*(S12m-
        S12f)+(A22+A32)*S11f+A11*S11m))+(A11*(A22+A32)-2*A12*A21)*(S11m)^2*Vm^2+S11f*Vf^2));
E(i)=E11C;
i=i+1;
end
ws=.02:.01:.06;
plot(ws,E/Em,'.-b');
xlabel('weight fraction of nanoclay in composite');
ylabel ('E_c/E_m');
```